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ENERGY TRANSFER IN PLANETARY ATMOSPHERES:
OPTICAL SPECTROSCOPIC STUDIES

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ABSTRACT

A cooperative program is in progress at the Optical Spectroscopy Laboratory of the Physics Department at the University of California, Santa Barbara and the Space Sciences Division of the Ames Research Center. It provides for graduate students and post-doctoral fellows to spend at least one-fourth of their time in a NASA laboratory and includes the possibility of Ames staff members carrying out specific research at UCSB. The research effort is in support of the on-going research programs both at UCSB and Ames concerning the reactions involving the constituents of planetary atmospheres. Initial studies are concerned with energy transfer mechanisms of importance to the understanding of the atmospheres of Mars and Venus.

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PART I
INTRODUCTION

Studies of reactions of gaseous molecules and atoms have been carried out using optical and mass spectrometers. These tools have been used at Ames Research Center, at the University of Colorado, and at the University of California at Santa Barbara to study properties of $O(^1D)$, CO_2 , CO_2^+ , and NO .

The use of a microwave powered helium lamp giving nearly monochromatic 58.4 nm radiation has made it possible to study the interaction of moderately high energy photons with gases found in planetary atmospheres. In particular, studies have been made of fluorescence of CO_2^+ by photoionization of CO_2 at 58.4 nm to measure cross sections for this process. Spectra obtained in this manner are similar to those of the Martian upper atmosphere obtained by Mariners 6 and 7. In addition, spectra of O_2^+ , CO^+ , N_2O^+ and N_2^+ have been obtained in the photoionization at 58.4 nm of O_2 , CO , N_2O , and N_2 respectively. In addition, reactions of $O(^1D)$ and fluorescence of NO γ bands have been measured.

One of the objectives of this program is to facilitate exchange of personnel and ideas between groups of atmospheric physicists. With this in mind two research assistants spent three months at Ames Research Center in California and one of them travelled to Boulder, Colorado, to work at the Laboratory for Atmospheric and Space Physics on the University of Colorado campus.

PART II

A. WORK AT AMES RESEARCH CENTER

T. S. Wauchop assisting Dr. W. Starr

A flowing afterglow system comprising a microwave discharge for producing the afterglow with a series of inlet jets for introducing reactants at set positions in the afterglow, and a quadrupole mass spectrometer was under construction. Between the afterglow tube and the mass spectrometer was a differential pumping system designed to reduce the pressure from that in the reaction tube to the operating pressure of the mass spectrometer.

This differential pumping system is comprised of three chambers separated by thin metal plates each with a small diameter hole (~ 1 mm) in the center. Each chamber was evacuated by a oil diffusion pump. Reaction products passing through the differential pumping chambers formed a beam entering the ionization chamber of the mass filter.

Construction and installation of the ion source, mass filter and particle detector of the mass spectrometer was completed, the mass spectrometer tuned so that mass number 28 of N_2^+ and CO^+ was almost resolved. A circular beam chopper was constructed and mounted in the second chamber of the differential pumping system. Used in conjunction with a lock-in amplifier, the chopper was intended to help in detection of small changes in concentration of reaction products.

T. Applebaum with Dr. M. Lowenstein

In an attempt to observe $O(^1D)$ in emission at 630.0 nm (the $^1D - ^3P$ transition) a flow of O_2 or CO_2 was passed through a photolysis cell irradiated with 147.0 nm light. The cell was observed with an 0.3 meter grating spectrometer and cooled photomultiplier. Repeated scans of the 630.0 nm region were summed using a multi-channel analyzer.

A positive identification of the 630.0 nm emission was not achieved. The photomultiplier was then combined with a

narrow pass band interference filter centered at 630.0nm. This photometer was made to scan over the 630.0nm region by repeated small rotations of the filter. Work was to proceed to measure rates of reactions of $O(^1D)$ with O_2 and CO_2 by observing the quenching of $O(^1D)$. Some of this work has been reported¹ and the method outlined has been successfully used by Noxon.²

B. WORK AT THE UNIVERSITY OF COLORADO

T. S. Wauchop

Fig. 1 shows a spectrum of the type obtained by Mariners 6 and 7 from the upper atmosphere of Mars. This spectrum is shown here by courtesy of Dr. C. A. Barth of the Laboratory for Atmospheric and Space Physics, Boulder, Colorado.³ The band systems as marked are the CO Cameron bands and the CO_2^+ A - X and B - X band systems. Also shown is the 297.2 nm line due to the $^1S - ^3P$ transition of atomic O.

Laboratory studies are being carried out to determine the cross sections for production of emission in the CO_2^+ A - X and B - X systems by photoionization of CO_2 using 58.4 nm radiation.

Helium is flowed through a microwave discharge at 1.2 Torr pressure. A 100nm thick aluminum filter is mounted on the end of the discharge tube 4 cm downstream so as light from the center of the discharge will pass through the filter. A grazing incidence spectrometer has been used to observe the radiation from the lamp, only the 58.4nm and 53.6 nm lines of helium are emitted at a ratio of 50 to 1. The 30.4 nm line of ionized helium is at least two orders of magnitude less intense than the 58.8 nm line. The intensity of the beam from the lamp has been measured by ion currents produced in H_2 or Argon by the 58.4 nm beam.

Carbon dioxide flowed slowly through a reaction chamber at 60 μ pressure. The lamp is mounted centrally on one end of the chamber which is 15 cm long and 15 cm diameter. Quartz windows mounted on the chamber make it possible to observe fluorescence at right angles to and directly facing the 58.4nm beam.

An 0.5 meter Fastie-Ebert monochromometer is used to observe the photoionization in the chamber. Figs. 2 and 3 show the CO_2^+ emissions observed in the first and second orders respectively. In fig. 2 the bottom trace is at 0.5 nm resolution while the top one is at 2.0 nm for comparison with the spectrum from Mariner in fig. 1. Similarly in fig. 3 the bottom trace is at 0.15 nm resolution and the top at 2.0 nm. Band heads are identified from the work of Judge et al⁵ and Mrozowski⁶. Assignments of unidentified bands have been made by extrapolation from the known systems. For example, the band at 371.1 nm is probably the $(2,0,0) \rightarrow (3,0,0)$ transition of the $^2\Pi_{1/2}$ system and bands at 426.8 and 427.8 nm are identified as the $(1,0,0) \rightarrow (5,0,0)$ transitions of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ systems respectively.

Several features are given identifications in the $(v_1', 0,0) \rightarrow (v_1'', 0,2)$ systems. The most intense of these bands are at 362.0 and 396.1 nm. These were first observed by Smyth [1931]. Following Judge et al [1969], they are identified as the $(4,0,0) \rightarrow (2,0,2)$ and $(3,0,0) \rightarrow (3,0,2)$ bands. At 363.8 nm is the $(5,0,0) \rightarrow (3,0,2)$ band which fits with the 1108 cm^{-1} energy for the fifth vibration of the $^2\Pi_{1/2u}$ electronic level. Likewise, features at 346.7, 347.3, 360.0, 361.2, 380.6 and 399.8 nm are identified as the $(3,0,0) \rightarrow (0,0,2)$, $(4,0,0) \rightarrow (1,0,2)$, $(2,0,0) \rightarrow (0,0,2)$, $(3,0,0) \rightarrow (1,0,2)$, $(5,0,0) \rightarrow (4,0,2)$ and $(5,0,0) \rightarrow (5,0,2)$ bands respectively.

A tungston lamp was used to obtain a absolute calibration of the monochromator and photomultiplier. This will give an absolute number for the photon emission of the fluorescence. Therefore it will be possible to calculate the cross sections for the production of emission in each of the CO_2^+ band system.

High energy photon bombardment of CO_2 is thought to be important in the Martian atmosphere⁷ and the cross sections obtained in this work will be useful in the construction of atmospheric models. In addition a comparison will be made of results of the photon excitation measurements with the some concurrent work in this laboratory with the same energy electrons.

Interaction of 58.4 nm radiation with other gases causes fluorescence. Band systems observed with N_2 , N_2O , NO , CO and O_2 are given in Table I. Similar cross sections will be measured for each of these systems.

Interaction of the uv radiation below 118.0 nm on CO₂ is known to produce 557.7 nm fluorescence.⁸ It is hoped to measure cross section for production of emission of 557.7 nm, the transition of O('S - 'D), using krypton 116.5 nm radiation. This will indirectly give a measure for the production of the O('D - ³P) line at 297.2 nm.

H. P. Broida

Fluorescence from the nitric oxide gamma system is a prominent feature of the near ultraviolet spectrum of the earth's atmosphere.⁹ In the laboratory the NO γ system has been excited both by the 214.4 nm line of ionized cadmium the 2138 line of Zinc and by a Xenon continuum source. A technique to calibrate a spectrometer between 200 nm and 250 nm has been developed using calculated branching ratios and comparison with irradiance and radiance standards. Measured relative vibrational band intensities from the line and from the continuum excitation are being compared to calculated Franck-Condon factors. In addition, polarization measurements are being made to an accuracy of 2%.

It is also hoped to carry out some work on trapping of ozone at a solid carbon dioxide surface during the photolysis of gaseous carbon dioxide. Ultraviolet solar radiation scattered from the southern polar cap of Mars and measured by a scanning monochrometer on the Mariner 7 spacecraft as passed near Mars in August, 1969, has shown the presence of ozone.³

C. WORK AT U.C.S.B

T. Applebaum with Dr. M. Manalis

Three computer programs for use with spectroscopic measurement and analysis were written and debugged. Instruction manuals also have been written to assist the user in operation of the programs. The usage of the programs are as follows:

1. The DATFIT package is a flexible main program for a

user-written code which finds the least squares optimum values for the parameters of any given (differentiable) mathematical description of the input data. It also returns standard errors and confidence intervals for the parameters, and a parameter correlation matrix.

The versatility of DATFIT is enhanced by the fact that the user supplies three subroutines in which he can do any data manipulation he desires. Provision is made for communicating between these subroutines through an array in COMMON.

The users model for the data is defined in one of his subroutines and may be any function, differentiable with respect to the adjustable parameters. The partial derivatives with respect to the parameters may be explicitly defined in the same routine, or calculated by finite differencing by the main program.

DAFIT originated as NLIN - "Least Squares Estimation of Non-Linear Parameters," a code by Baumeister and Marquardt.¹⁰

The description of NLIN is more detailed than the present manual and is invaluable for understanding DATFIT.

2. TEMP is a computer program which facilitates the recognition of a Boltzmann population distribution among observed energy levels. It performs a linear least squares fit of the log of population vs energy. TEMP is applicable both to atomic and molecular levels.

As it often occurs that one distribution, at a single temperature, is inadequate to describe the population density over the entire energy domain, thus provision is made for ignoring certain levels in fitting the Boltzmann distribution. This technique is also useful in assessing bad data points. As many as five alternative fits may be performed for a single set of data.

The printed output includes level populations, and the temperature for each alternative, together with its standard error. The log of population from the input data is plotted vs energy, as are the theoretical curves.

Optional punched output includes the energy and log of population, suitable for use as data by the DATFIT program.

Images of some of the input data may also be punched for use in running new cases of TEMP.

3. RELENS is a computer code which calculates the relative sensitivity of an optical system as a function of wavelength, given the calibrated intensity distribution of the standard lamp and an intensity distribution observed through the system.

A graph of relative sensitivity vs wavelength may be generated and sensitivities at particular wavelengths may be obtained by linear interpolation of the data.

In addition RELENS can punch cards of relative sensitivity and wavelength in TEMP format.

The user-supplied subroutine SENS permits the user to input his observed spectrum in units other than those of the standard lamp spectrum. SENS may then be called on to convert the data.

FIGURE CAPTIONS

- Fig. 1. Spectrum obtained by Mariner space probes of fluorescence in the Martian upper atmosphere.
- Fig. 2. First order spectrum of $\text{CO}_2^+ \tilde{\text{A}} - \tilde{\text{X}}$ and $\tilde{\text{B}} - \tilde{\text{X}}$ systems at resolution of 0.5 nm, showing bands at longer wavelengths.
- Fig. 3. Second order spectra of $\text{CO}_2^+ \tilde{\text{A}} - \tilde{\text{X}}$ and $\tilde{\text{B}} - \tilde{\text{X}}$ systems. Lower spectrum at a resolution of 0.15 nm; upper spectrum at a resolution of 2.0 nm for comparison with Mariner spectra.

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TABLE I.

<u>Molecule</u>	<u>Observed Bands</u>		<u>v'</u>
N ₂	N ₂ ⁺	B ² Σ _u ⁺ → X ² Σ _g ⁺	0 - 2
	N ₂	C ³ Σ _u ⁺ → B ³ Π _g	0
NO	NO	A ² Σ ⁺ → X ² Π	0,1
N ₂ O	N ₂ O ⁺	A ² Σ ⁺ → X ² Π	0,1
O ₂	O ₂ ⁺	b ⁴ Σ _g ⁻ → a ⁴ Π _u	0 - 2
CO	CO ⁺	A ² Π → X ² Σ ⁺	0 - 6
		B ² Σ ⁺ → X ² Σ ⁺	0,1
		B ² Σ ⁺ → A ² Π	0,1

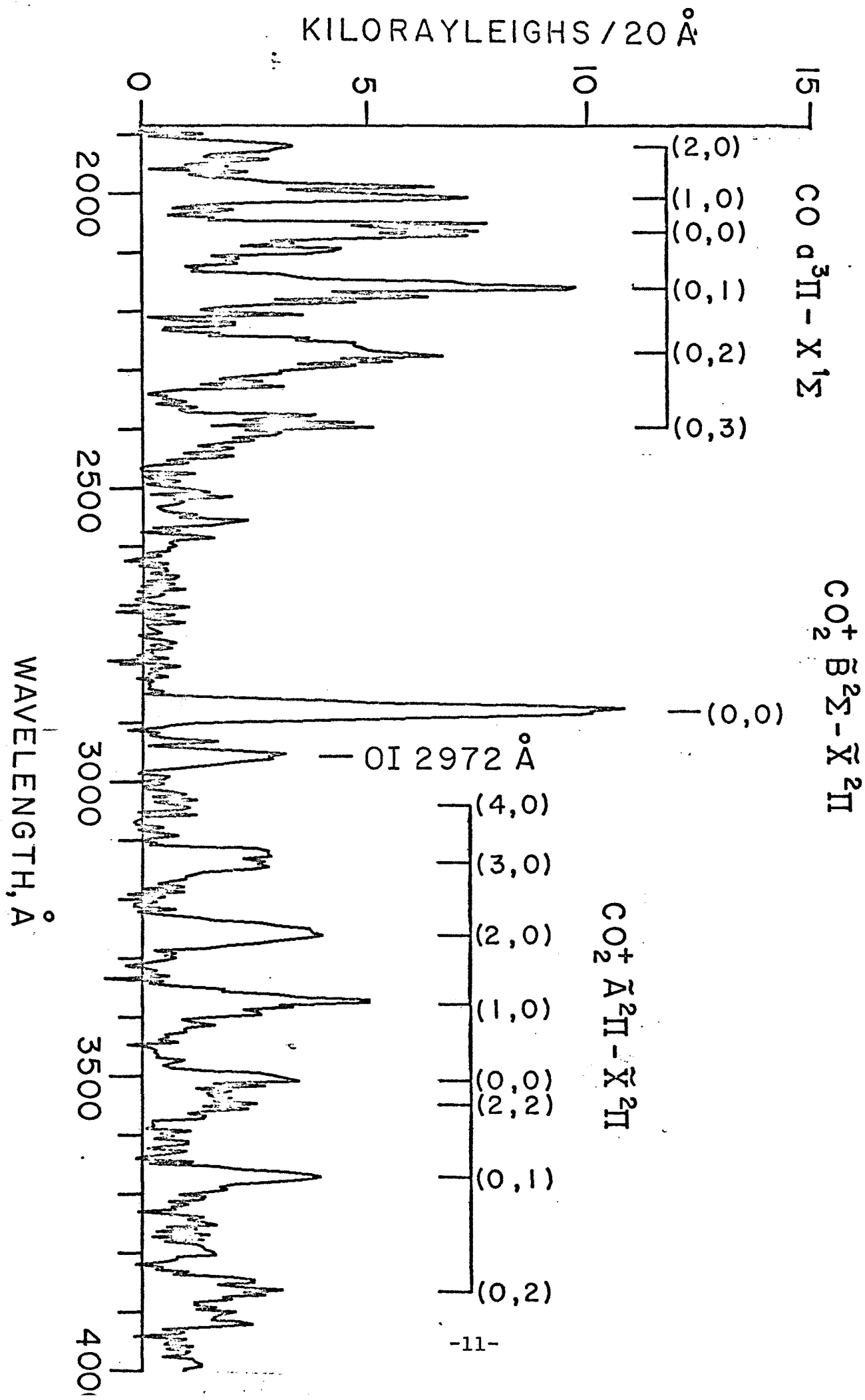


Fig. 1

fig. 2

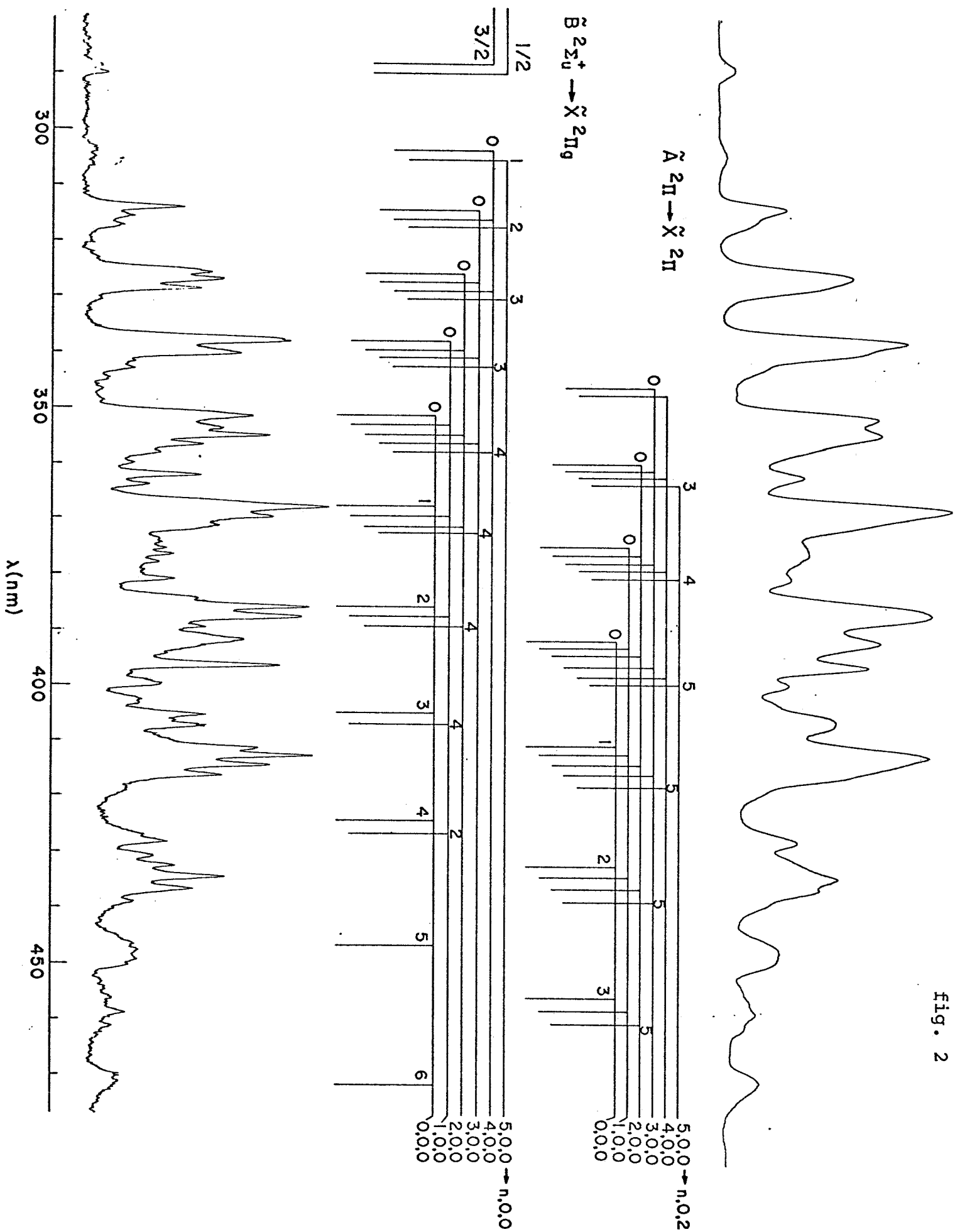
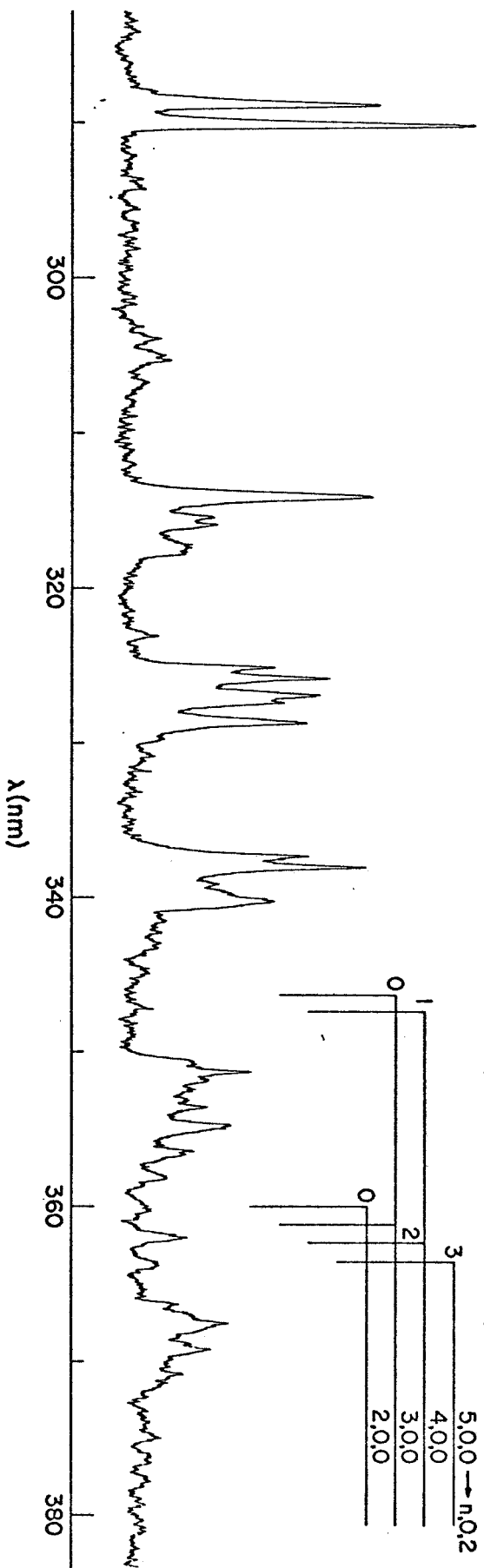
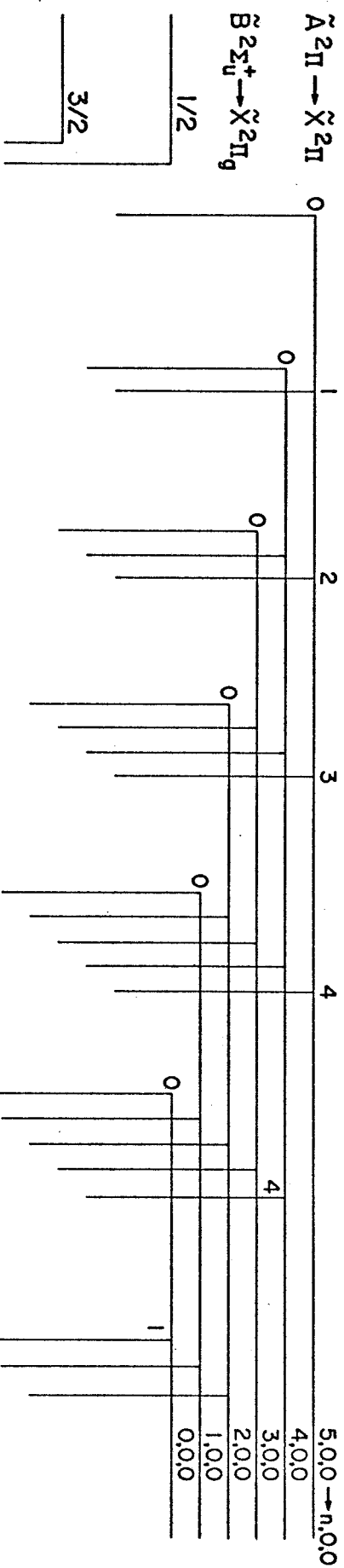
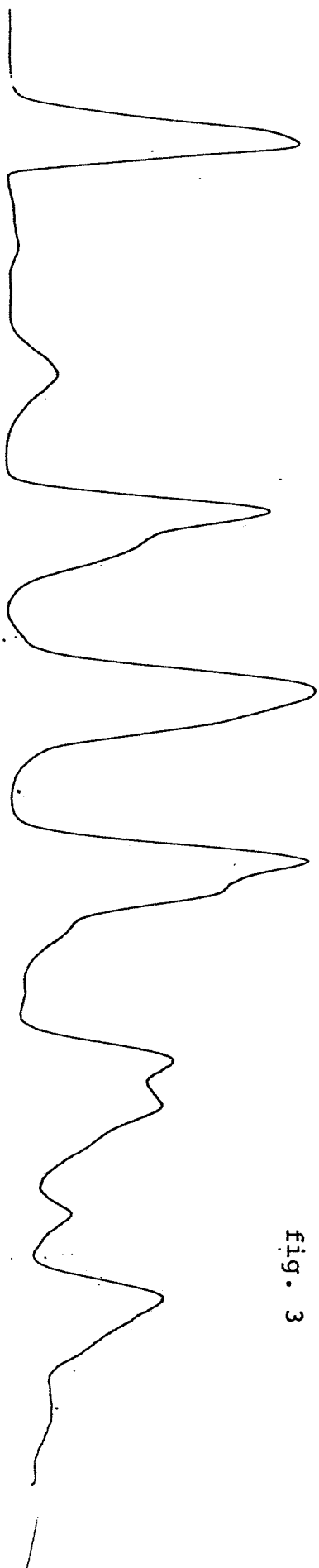


fig. 3



INVITED LECTURES AND PAPERS

Title	Author	Date and Location
The Interpretation of the Ultraviolet Spectra of Mars from Mariner 6	H. P. Broida	8/69, Ninth Free Radical Symposium, Bannf, Canada
Ultraviolet Spectroscopy of Planetary Atmospheres	H. P. Broida	12/69, NBS Gaithersburgh
Rocket and Satellite Ultraviolet Spectroscopy	H. P. Broida	4/70, Canadian Assoc. of Physics, Toronto, Canada
Ultraviolet Spectroscopy of the Atmosphere of Mars (Invited paper)	H. P. Broida	5/70, Symposium on Analytical Chemistry i Space Exploration, American Chemical Society/ Chemical Institute of Can. Toronto Canada
An Outsiders View of the Ultraviolet Spectra of Mars	H. P. Broida	5/70, Joint Institute of Laboratory Astrophysics, Univ. of Colorado, Boulder